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A METHOD OF EXTRACTING METAL PALLADIUM

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A METHOD OF EXTRACTING METAL PALLADIUM

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Claims /1

1. A method of extracting metal palladium by adding reagents to a solution containing palladium and separating the reaction product after reaction, followed by carrying out normal treatment on the reaction product to give metal palladium, characterized in that the reactant added in the solution containing palladium is alkaline metal iodides, which react with palladium to form palladium diiodide.

2. The method according to the description in Claim 1, characterized in that the added alkaline metal iodide is potassium iodide.

3. The method according to the description in Claim 2, characterized in that said reagents also comprise inert organic solvent, and that the product gets into the organic layer after reaction.

* [Numbers in the right margin indicate pagination of the foreign original text.]

4. The method according to the description in Claim 3, characterized in that the acidity of the reaction system is from pH 12 to 7.2 mol/liter [sic].

5. The method according to the description in Claim 4, characterized in that the inert solvent is nitrobenzene.

6. The method according to the description in Claim 4, characterized in that the inert solvent is bromobenzene.

7. The method according to the description in Claim 4, characterized in that the inert solvent is chlorobenzene.

8. The method according to the description in Claim 4, characterized in that the inert solvent is petroleum ether.

9. The method according to the description in Claim 4, characterized in that the inert solvent is chloroform.

10. The method according to the description in Claim 4, characterized in that the inert solvent is liquid paraffin.

11. The method according to the description in Claim 4, characterized in that the inert solvent is kerosene.

12. The method according to the description in Claim 4, characterized in that the inert solvent is toluene.

13. The method according to the description in Claim 4, characterized in that the inert solvent is xylene.

14. The method according to the description in Claim 4, characterized in that the inert solvent is benzene.

15. The method according to the description in Claim 4, characterized in that the inert solvent is a mixture of nitrobenzene, bromobenzene, chlorobenzene, petroleum ether, chloroform, liquid paraffin, kerosene, benzene and xylene.

16. The method according to the description in any of Claims 1-15, characterized in that said reagents also comprise crown ether.

17. The method according to the description in Claim 16, characterized in that the crown ether solution is made to contact with potassium iodide to form crown ether-potassium iodide extracting complex and that this extracting complex is then reacted with the material solution.

18. The method according to the description in Claim 17, characterized in that the palladium diiodide obtained from the reaction is eluted with ammonia water and that electrolysis is conducted on the resulting aqueous phase.

19. Palladium diiodide, characterized in that it is produced by any of the methods according to the description in Claims 1-17.

20. A production method of iodine, characterized in that the method according to the description in Claim 18 is employed.

21. Iodine, characterized in that it is produced by any of the methods according to the description in Claim 18 [sic; Claims 1-18].

22. Palladium, characterized in that it is produced by any of the methods according to the description in Claims 1-18.

Description

The present invention pertains to a method of extracting metal palladium. The present invention consists of adding reagents to a solution containing palladium, particularly radioactive waste liquid containing palladium, and isolating the reaction product after reaction, followed by conducting normal treatment methods on the reaction product to give metal palladium. Here, said normal treatment methods mean treatment methods such as reverse extraction, electrolysis or displacement among conventional techniques.

In conventional technology, extraction by TBP, amines or quaternized ammonium salts or reduction-precipitation treatment is generally performed in a sulfuric acid or hydrochloric acid solution system containing palladium, and the product is isolated and further purified after reaction, followed by electrolysis or carrying out displacement treatment to give metal palladium. The drawbacks of the conventional techniques are low selectivity and long treatment duration, while there are also restrictions for some processes on the acidity of the material solution as well as low extracting efficiency. In addition to the above drawbacks, the conventional techniques also have an unsatisfactory treatment effect for radioactive nuclear waste liquid.

In the treatment methods of radioactive nuclear waste liquid containing palladium, the reduction-precipitation method is in general considered a method with high development potential. [He Huaxue Yu Fangse Huaxue (Nuclear Chemistry and Radiation Chemistry)], 8(3), 147 (1986) and [Chin. Z. Nucl. Sci. Eng.], 6(3), 233 (1986) disclosed a treatment method where palladium, ruthenium and rhodium were precipitated in metal form during a formate-denitration process, followed by carrying out purification process. U.S. Patent No 4,290,267 disclosed a palladium precipitation method by sucrose denitration. Both of the above methods required reactions with boiling and long reaction time of more than a few hours, in that the reducing agents were mostly consumed in nitration, while also producing large quantities of nitrogen and carbon dioxide; also, the products were mixtures of ruthenium and rhodium, which must be stored for a few dozen years before they can be used without protecting measures.

The objective of the present invention lies in providing a method of extracting metal palladium, with the advantages of convenience, fast process, high recovery rate, good selectivity and low waste, to overcome the drawbacks of the conventional techniques, and the other

objective of the present invention lies in providing a method of obtaining iodine in the meantime while extracting metal palladium.

The objective of the present invention is achieved via the following measures:

Inert solvent and alkaline metal iodide are added to a solution containing palladium to react with the palladium and form palladium diiodide. The product is collected through the organic phase, whereas the collection means that the product enters or is mixed in the organic phase, and after isolation, treatment methods of conventional techniques such as reverse extraction, electrolysis of displacement are conducted to give metal palladium.

The objective of the present invention is also achieved via the following measures:

The added alkaline metal iodide is potassium iodide and said inert solvent is nitrobenzene, bromobenzene, chlorobenzene, petroleum ether, chloroform, liquid paraffin, kerosene, benzene, toluene or xylene, or a mixture thereof.

The added reagents also comprise crown ether in order to extract the palladium complex ion formed with the excessive amount of potassium iodide.

The material solution of the present invention comprises a sulfuric acid solution containing palladium or a nitric acid solution containing palladium or a hydrochloric acid solution containing palladium, and said material solution may be a normal smelting material solution or radioactive nuclear waste liquid.

For an acidic solution containing palladium, the crown ether solution is first made to contact with potassium iodide to prepare a crown ether-potassium extracting complex, followed by reacting this extracting complex with the material solution.

The palladium diiodide obtained from the aforementioned method is then eluted with ammonia water, followed by electrolysis of the aqueous phase, and in the meantime, iodine is obtained.

The key reactions carried out by the present invention comprise: reacting palladium in the material solution with potassium iodide to form palladium diiodie, in that the part of the precipitates that are soluble [sic; insoluble] in water is collected by the inert solvent, and when there is excessive potassium iodide, the palladium complex ion is extracted by crown ether. Said precipitation, collection and extraction processes are macroscopically regarded as an extracting method. The reaction equations of the aforementioned reactions are as follows:

/2

/3

$$Pd(II) + 2MI = 2M^{+} + PdI_{2(s)}\downarrow \quad (1)$$

$$PdI_{2(s)} = PdI_{2(o)} \quad (2)$$

$$PdI_{2(s)} = PdI_{2(w)} \quad (3)$$

$$Pd(II) + 4MI = M_2PdI_4 + 2M^{+} \quad (4)$$

$$M_2PdI_4 + 4L = [ML_2]_2PdI_4 \quad (5)$$

$$2M_2PdI_4 + 4L = [ML_2]_2Pd_2I_6 + 2MI \quad (6)$$

Where in the aforementioned equations, M is alkaline metal, L is crown ether; the lower case (o) means organic phase, the lower case (w) means aqueous phase, and the lower case (s) means solid phase.

The above equations indicate that metal palladium can be conveniently obtained from the palladium diiodide in the present invention by employing an electrolysis or displacement method of the conventional techniques.

The measures utilized to achieve the present invention can also be further clarified using the experimental data shown below, and the material solution utilized in said experiment comprise 4 kinds, the 1st kind being high concentration nitric acid and high concentration material solution 1 containing palladium; the 2nd kind being high concentration nitric acid and low concentration material solution 2 containing palladium; the 3rd kind being alkaline material solution 3; the 4th kind being material solution 4 with hydrochloric acid or sulfuric acid medium. Appendixes 1, 2 and 3 show the specific compositions of the aforementioned material solutions. The first 3 kinds of experimental material solutions were radioactive, which were typical nuclear waste liquids, while the 4th kind was a normal smelting material solution. The basic process of these experiments was adding inert solvent and potassium iodide to a material solution, or adding crown ether, agitating, isolating organic phase after reaction, electrolysis of the aqueous phase after eluting the organic phase with ammonia water, to finally obtain metal palladium and iodine. The common conditions of the experiments are: the reaction is conducted at room temperature, while the (reaction) temperature for the following experimental data is 15°C unless otherwise specified.

The specific experimental data are shown in the following tables, where E stands for rate of extraction:

Table 1. Effect of mole ratio of potassium iodide and palladium in material solution containing nitric acid

Qa/Qp	0	50	100	150	200	250	300	350
E, %	89.7	98.1	99.5	99.3	99.1	98.5	90.1	90.1

* Except for changing the mole Qa of added potassium iodide, all the conditions are the same as that of Table 2. Among them, Qp is the moles of palladium in the material solution (same hereafter).

Table 2. Result of palladium extraction from high concentration nitric acid system using various inert solvents

① 溶剂	E, %	溶 ① 剂	E, %
② 硝基苯	99.2	氯 ③ 代苯	94.8
④ 溴代苯	98.1	氯 ⑤ 仿	93.0
⑥ 石油醚	95.0	二 ⑦ 甲苯	95.1
⑧ 石腊油	92.0	甲 ⑨ 苯	93.2
⑩ 煤油	97.0	⑪ 苯	92.7

⑫ • 实验条件：在10.00毫升含2.084×10⁻⁴m ol/l钯和3.16mol/l 硝酸的料液中加10.00毫升有机溶剂。在搅拌条件下加入2.00毫升0.40mol/l的碘化钾。

Key:
1 Solvent
2 Nitrobenzene
3 Chlorobenzene
4 Bromobenzene
5 Chloroform
6 Petroleum ether
7 Xylene

8 Liquid paraffin
9 Toluene
10 Kerosene
11 Benzene
12 * Experimental condition: Organic solvent 10.00 mL was added to 100 mL material solution containing 2.084×10^{-4} mol/L palladium and 3.16 mol/L nitric acid. 2 mL of 0.40 mol/L potassium iodide was added while agitating.

Table 3. Effect of mole ratio R of B15C5-potassium iodide extracting complex and palladium in material solution containing nitric acid on rate of extraction of palladium

R	0	37.6	77.0	154	230	308	385	460
E, %	69.4	89.3	96.2	99.2	99.7	99.7	99.6	96.0

* The solvent was nitrobenzene, and all conditions were the same as that of Table 2.

Table 4. Relationship of concentration of crown ether in crown ether-potassium extracting complex and that of potassium iodide

体 ① 系	A	B	B	D
②冠醚浓度 ($10^{-[illegible]}$) mol/l	5.00	5.08	1.23	1.56
碘化钾浓度 ③ ($10^{-[illegible]}$) mol/l	2.49	2.56	1.23	1.57

④ 表中的A为B15C5-$CHCl_3$
B为B15C5-$C_6H_5NO_2$
C为DB18C6－C_6H_5Br
D为DB18C6－$C_6H_5NO_2$

⑤ • B15C5和DB18C6 分别为苯并-15-冠-5和二苯并-18-冠-6。

⑥ 实验条件：冠醚溶液与中性的饱和碘化钾溶液接触，相比1：1. 表中碘化钾的浓度为它在萃合物有机相中的浓度。

Key:
1. System
2. Crown ether concentration
3. Potassium iodide concentration
4. Where in the table, A is B15C5-$CHCl_3$
   B is B15C5-$C_6H_5NO_2$
   C is DB18C6-C_6H_5Br
   D is DB18C6-$C_6H_5NO_2$
5. B15C5 and C is DB18C6 are benzo-15-crown-5 and dibenzo-18-crown-6, respectively.
6. Experimental condition: The crown ether solution was made in contact with a neutral and saturated solution of potassium iodide, with a phase ratio of 1:1. The concentration of potassium iodide in the table was its concentration in the organic phase of the extracting complex.

Table 5. Effect of mole ratio of potassium iodide and palladium in material solution containing nitric acid on rate of extraction

Qs/Qp	2.0	3.6	5.4	8.0	10.8	14.0	17.6	20.0	24.0
E, %	60.0	82.1	94.2	98.4	98.5	97.4	98.1	88.0	47.6

* Nitrobenzene 1.00 mL was added to 10.00 mL palladium material solution (in that the palladium concentration was 2.20×10^{-2} mol/L and the nitric acid concentration was 3.52 mol/L), and 1.00 mL of potassium iodide of various concentrations was added under agitation. /6

Table 6. Effect of mole ratio R of B15C5-potassium iodide extracting complex and palladium in material solution containing nitric acid on rate of extraction

R	2.0	4.0	6.0	10.0	12.0	14.8	18.8	3.25
E, %	74.1	89.0	98.5	99.0	98.7	99.8	98.0	89.0

* 10.00 mL of I- B15C5-nitrobenzene of various concentrations was added to 10.00 mL material solution, in that the palladium concentration in the material solution was 2.2×10^{-2} mol/L and the nitric acid concentration was 3.52 mol/L.

Table 7. Result of palladium extraction from alkaline material solution using various inert solvents

溶 ① 剂	E, %	溶 ① 剂	E, %
$CHCl_3$	5.5	C_6H_6	8.0
$C_6H_5CH_3$	16.9	$C_6H_5NO_2$	91.0
C_6H_5Cl	21.5	C_6H_5Br	10.0
C_6H_5I	31.2	石腊油 ②	0
煤 油 ③	0		

Key: 1 Solvent
2 Liquid paraffin
3 Kerosene
4 * The material solution contained 1.73×10^{-4}mol/l palladium, pH=10.2, potassium iodide was 0.08mol/l and the phase ratio was 1:1.

Table 8. Effect of mole ratio Qa/Qp of potassium iodide and palladium in material solution on extraction of palladium with nitrobenzene

Qa/Qp	0	87	173	347	462	694	1387
E, %	62.0	80.3	91.0	91.0	91.3	90.6	84.1

* The material solution contained 1.73×10^{-4} mol/L palladium, pH=10.2

Table 9. Effect of pH of material solution on extraction of palladium with B15C5-nitrobenzene

pH	12.1	12.1	11.8	11.6	11.3	10.6	8.16
E, %	0	0	92.2	92.7	94.7	95.6	94.6

*

In 10.00 mL material solution, Pd=1.76x10^{-4} mol/L and KI=0.08 mol/L, and the supernatant reacted with 10.00 mL B15C5-nitrobenzene (the concentration was 2.484x10^{-3} mol/L).

Tabie 10. Effect of Qa/Qp on extraction of palladium with B15C5-nitrobenzene

Qa/QP	75	150	300	450	600	900	1500	3000	6000	7500
E, %	93.0	97.1	96.4	95.9	96.1	96.4	94.9	80.7	67.5	62.7

*

10.00 mL material solution (containing 1.31x10^{-4} mol/L palladium and 0.20 mol/L potassium iodine, pH was 10.2) reacted with 10.00 mL B15C5-nitrobenzene (2.484x10^{-3} mol/L).

Table 11. Effect of mole ratio (B:Pd) of added amount of B15C5 and palladium in material solution on extraction of palladium

B : Pd	56.0	41.0	21.0	10.0	4.4	1.7
E, %	96.3	96.1	96.1	96.8	94.8	96.3

* The organic solvent of this experiment was nitrobenzenen, and the material solution contained 1.13x10^{-4} mol/L and 0.12 mol/L potassium iodide, pH was 10.2 and the phase ratio was 1:1.

Table 12. Effect of ammonia water concentration on rate of palladium elution

① 浓氨水：水	1：0	2：1	1：1	1：2	1：9
E，%	98.2	100	100	97.5	89.4

② * 料中含钯8.66×10⁻⁴mol/l，碘化钾0.4 mol/l，pH值为 10.2，经用2.484×10⁻³mol/l 的B15C5-硝基苯按相比1：1萃取后，96.1 %的钯进入有机相，然后用此有机相做洗脱实验，洗脱相比为1：1，实验温度为18℃。

Key: 1 Concentrated ammonia water:water
2 * The material solution contained 8.66×10^{-4} mol/L palladium and 0.4 mol/L potassium iodine, pH was 10.2, and via extracting with 2.484×10^{-3} mol/L B15C5-nitrobenzene at phase ratio 1:1, 96.1% of the palladium entered into the organic phase, and the organic phase was subjected to elution experiment, with elution phase ratio of 1:1 and experimental temperature of 18°C.

Table 13. Result of electrolysis of crude product

① 电压，V	2	6	12	18
② 钯收率，%	96	97	96	96
③ 碘收率，%	86	83	83	80

④ * 用洗脱的水溶液进行电解，其中水溶液含钯5.6×10⁻²mol/l，电解时间未控制一致，而以水相变为无色为限，钯的收率由测定电极上刮下的钯确定；碘的收率由残余水相的体积和碘的浓度求得。

Key: 1 Voltage
2 Palladium yield
3 Iodine yield
4 * Electrolysis was conducted on the aqueous solution from elution, in that the aqueous solution contained 5.6×10^{-2} mol/L palladium, and the time of electrolysis was not controlled but judged from the color change of the aqueous phase until becoming colorless, and the palladium yield was determined from the amount of palladium scratched from the testing electrode; the iodine yield was obtained from the volume of residual aqueous phase and the concentration of iodine.

Table 14. Effect of radioactive radiation on yield

① 辐照	剂量率, 10^3 Gy · h^{-1} ②	1.2	2.1	7
剂量	总剂量, 10^3 Gy · h^{-1} ③	1.0	4.9	11.0
④ 收率	a 组实验 ⑤	99.3	96.5	89.0
E, %	b 组实验 ⑥	99.0	96.0	90.5

⑦ * 表中：

a组试验：10.00毫升料液（含钯2.20×10^{-2}mol/l，硝酸3.52mol/l）中加1.00毫升的硝基苯，搅拌条件下加1.00毫升1.64mol/l的碘化钾，然

Key:
1 Radiation dose
2 Dosing rate
3 Total dose
4 Yield
5 Group a experiment
6 Group b experiment
7 * In the table:

Group a experiment: Nitrobenzene 1.00 mL was added to 10.00 mL material solution (containing 2.20×10^{-2} mol/L palladium and 3.52 mol/L nitric acid), and 1.00 mL of 1.64mol/l potassium iodide was added under agitation, followed by subjecting to irradiation. /1

Group b experiment: 0.328 mol/L B15C5-nitrobenzene was made in contact with the same volume of saturated potassium iodide solution, and after reaching equilibrium, the phases were separated, and 10.00 mL of said organic phase was added to 10.00 mL material solution (containing 2.20×10^{-2} mol/L palladium and 3.52 mol/L nitric acid) and agitated for 1 min, followed by subjecting to irradiation.

Table 15. Experimental result in hydrochloric acid medium

① 收率 E，%				
c ② 组	91.2	-	-	-
d ② 组	97.7	98.1	98.3	96.8

③ * c组实验：10.00毫升料液（钯含量为2.048×10⁻⁴mol/l，碘化钾为0.08mol/l，盐酸为7.2mol/l）与10.00毫升的B15C5-氯仿（1.5×10⁻³mol/l）反应。温度为20℃。

d组实验：10.00毫升料液（钯含量为2.048×10⁻⁴mol/l，盐酸为7.2mol/l）与10.00毫升的载饱和碘化钾的B15C5-氯仿（1.5×10⁻³mol/l）反应。水料中不加碘化钾。温度为20℃。

Key: 1 Yield
2 Group
3 * Group c experiment: 10.00 mL material solution (containing 2.048×10^{-4} mol/L palladium and 0.08 mol/L potassium iodide and 7.2 mol/L hydrochloric acid) was reacted with 10.00 mL B15C5-chloroform (1.5×10^{-3} mol/L). Reaction temperature was 20°C.
Group d experiment: 10.00 mL material solution (containing 2.048×10^{-4} mol/L palladium and 7.2 mol/L hydrochloric acid) was reacted with 10.00 mL B15C5-chloroform (1.5×10^{-3} mol/L) carrying saturated potassium iodide. No potassium was added in the feed water. Reaction temperature was 20°C.

Table 16. Experimental result in sulfuric acid medium

① 提取率	e ② 组	f 组②
E，%	95.1	98.9

③ * e组实验：10.00毫升料液（钯含量为2.074×10^{-4}mol/l，碘化钾为0.08mol/l，硫酸为3.0mol/l）与10.00毫升的B15C5-氯仿（1.50×10^{-3}mol/l）反应，温度为20℃。

f组实验：10.00毫升料液（钯含量为2.074×10^{-4}mol/l，硫酸为3.0 mol/l）与10.00毫升的载饱和碘化钾的B15C5-氯仿（1.50×10^{-3}mol/l）反应。水料中不加碘化钾。温度为20℃。

Key:
1 Extracting yield
2 Group
3 * Group e experiment: 10.00 mL material solution (containing 2.074×10^{-4} mol/L palladium and 0.08 mol/L potassium iodide and 3.0 mol/L sulfuric acid) was reacted with 10.00 mL B15C5-chloroform (1.50×10^{-3} mol/L). Reaction temperature was 20°C. /1

Group f experiment: 10.00 mL material solution (containing 2.074×10^{-4} mol/L palladium and 3.0 mol/L sulfuric acid) was reacted with 10.00 mL B15C5-chloroform (1.5×10^{-3} mol/L) carrying saturated potassium iodide. No potassium iodide was added in the feed water. Reaction temperature was 20°C.

Table 17. effect of solvent on extracting rate

实验 ① 组别	② 收率 E, %			
	③ 溶剂Ⅰ	③ 溶剂Ⅱ	③ 溶剂Ⅲ	③ 溶剂Ⅳ
g组 ④	96.0	98.7	94.7	96.8
h组 ④	97.3	99.8	96.0	98.4

⑤ • 溶剂Ⅰ为氯仿－煤油：Ⅱ为硝基苯－煤油：Ⅲ为溴苯－煤油：Ⅳ为氯仿－氯苯。

⑥ 它们的体积比（前物比后物）均为1比9。料液含钯2.084×10^{-4} mol/l和硝酸3.16mol/l，g类实验用无冠醚的溶剂，h类实验用含DB18C6为1.03×10^{-3}mol/l的有机溶剂，g和h两类实验的相比均为1比1。

Key:
1. Experimental group
2. Yield
3. Solvent
4. Group
5. Solvent I was chloroform-kerosene; solvent II was nitrobenzene-kerosene; solvent III was bromobenzene-kerosene; solvent IV was chloroform-chlorobenzene.
6. The volume ratio (ratio of the former to the latter) was all 1:9. The material solution contained 2.084×10^{-4} mol/L palladium and 3.16 mol/L nitric acid, and solvents without crown ether were utilized in group g experiment while organic solvents containing 1.03×10^{-3} DB18C6 were utilized in group h experiment, whereas the phase ratio was 1:1 for both group g and group h experiments.

Table 18. Effect of reaction time on extracting rate of palladium

① 提取率 E, %	提取时间 ②	
	50分钟③	150分钟 ③
直接提取 ④	99.1	83.4
加有机溶剂提取 ⑤	99.8	95.9
加含碘化钾的B15C5冠醚提取 ⑥	99.6	96.4

⑦ • 钯为2.20×10⁻²mol/l，硝酸为3.52mol/l,KI：Pd为7：1，有机相与水相的体积比为1：1，有机溶剂均为硝基苯.

本发明的优点如下:

Key:
1 Extracting rate
2 Extracting time
3 Min
4 Direct extraction
5 Extraction by adding organic solvent
6 Extraction by adding DB18C6 containing potassium iodide
7 Palladium was 2.20×10^{-2} mol/L and nitric acid was and 3.52 mol/L, and KI:Pd was 7:1, and volume ratio of organic phase to aqueous phase was 1:1, whereas the organic solvent was nitrobenzene in all cases.

The advantages of the present invention are as follows:

1. The present invention has broad application areas, and it is applicable in acidic solution, as well as applicable in alkaline solution; it can be utilized in treating smelting materials as well as in treating nuclear wastes.

2. The present invention exhibit high selectivity to palladium, and because the product obtained by the present invention has very high purity, the after treatment is easy.

3. The present invention has short production period, requiring only a few minutes for acquiring palladium diiodide from the reaction of a material solution.

4. The reaction of the present invention can be conducted at room temperature, and compared with conventional techniques, the present invention has lower energy consumption.

5. The potassium iodide utilized in the present invention can be recovered as iodine, which reduces production cost.

6. The yield of the present invention is high, which is validated by the application examples shown below.

7. The reaction system basically does not change during the reaction, and therefore, no additional pollution is produced by the present invention.

8. The method of the present invention minimizes exposure to radioactivity. /1

A few of the best application examples are shown in the following:

Application Example 1

Nitrobenzene 2.5 mL was added to 25 mL material **1**, to which 2.5 mL potassium iodide (1.64 mol/L) was added while agitating, and after agitating for 1 min, the aqueous phase was separated and the extracting rate was determined to be 98.1±0.5% from the palladium concentration in the aqueous phase, where the total volume of the aqueous phase was given as 27.5 mL. The precipitates were washed twice with 25 mL (3.52 mol/L) nitric acid. The results of spectral quantification after drying and cineration is as follows:

Pd being the key component, Sr 0.1%, Rh 0.003%, Ru 0.001%, Zn 0.001%

The other 11 co-existing elements in the sample solution were all undetectable.

Application Example 2

Bromobenzene 1.0 mL was added to 10 mL material **1**, to which 1.0 mL potassium iodide (1.64 mol/L) was added while agitating, and after agitating for 1 min, the aqueous phase was separated and the extracting rate was determined to be 96.5% from the palladium concentration in the aqueous phase, where the total volume of the aqueous phase was given as 11.0 mL.

Application Example 3

Bromobenzene 1.0 mL was added to 10 mL material **1**, to which 1.0 mL potassium iodide (1.68 mol/L) was added while agitating, and after agitating for 1 min, the aqueous phase was separated and the extracting rate was determined to be 95.0% from the palladium concentration in the aqueous phase, where the total volume of the aqueous phase was given as 11.0 mL.

Application Example 4

B15-C5-nitrobenzene solution 30 mL (0.328 mol/L) was made in contact with 10 mL potassium iodide for 20 min, and after phase separation by centrifuge, 25 mL of the organic phase (containing **I**-crown ether extracting complex) was taken and added to 25.00 mL material **1**, and after agitating for 1 min, the aqueous phase was separated, and the extracting rate was determined to be 98.3±0.5% from the palladium concentration in the aqueous phase. The precipitates were washed twice with 25 mL (3.52 mol/L) nitric acid. The results of spectral quantification after drying and cineration is as follows:

Pd being the key component, Sr 0.01%, Rh 0.0003%, Ru < 0.001%, Zn < 0.001%

The other 11 co-existing elements in the sample solution were all undetectable.

Application Example 5

25 mL Organic phase containing precipitates was prepared in accordance with the procedure of Application example 4, and the extracting rate was determined to be 98.0±0.4%. The palladium on the precipitates was washed twice with equal volume of ammonia water, and the eluting solutions were combined, which was concentrated by 2-fold after heating to eliminate ammonia, followed by electrolysis at 12-volt voltage using 2 Pt electrodes of 1 cm^2. Palladium deposited on the cathode and adhered to the electrode; iodine deposited on the anode and flowed automatically to the bottom of a receiving container. After the color of the mother liquid completely faded, the electrode was removed and the palladium was scratched off, and the entire palladium was added to aqua regia, and after the nitric acid was removed with hydrochloric acid, the amount of palladium was determined, giving a calculated electrolytic recovery rate of 94.5%; the remaining mother liquid was subjected to centrifuge separation, and the supernatant aqueous phase was isolated at the apparent dividing line, for which the volume was verified and the iodine concentration was determined, and the calculated iodine recovery rate was ~80%. /1

Application Example 6

Nitrobenzene 10.00 mL was added to 10 mL material **2**, to which 1.0 mL potassium iodide (0.40 mol/L) was added while agitating, and after agitating for 1min, the aqueous phase was separated and the residual palladium concentration in the aqueous phase was determined, and from which the extracting rate of palladium was calculated to be 98.4%.

Application Example 7

10.00 mL of 0.080 mol/L B15C5-nitrobenzene carrying saturated potassium iodide was added to 10 mL material **2**, and after agitating for 1 min, the aqueous phase was separated and the residual palladium concentration in the aqueous phase was determined, and from which the

extracting rate of palladium was calculated to be 99.0%; the palladium in the organic phase was eluted with equal volume of ammonia water to determine the palladium concentration in the obtained eluted solution, from which the eluting rate of palladium was found to be 97.2%.

Application Example 8

Same operation was conducted as the process in application example 7, except 10.00 mL of 0.040 mol/L DB18C6-nitrobenzene carrying saturated potassium iodide was added to material **2**, and after agitating for 1 min, the aqueous phase was separated and the residual palladium concentration in the aqueous phase was determined, and from which the extracting rate of palladium was calculated to be 98.5%; the palladium in the organic phase was eluted with equal volume of ammonia water to determine the palladium concentration in the obtained eluted solution, from which the eluting rate of palladium was found to be 98.2%.

Application Example 9

0.72 mL of 1.50×10^{-2} mol/L sodium hydroxide was added to 10 mL material **3** to give a pH of 10.2 for the material solution, to which 10.00 mL nitrobenzene was added, followed by adding 1.00 mL of 0.20 mol/L potassium iodide while agitating, and after agitating for 1 min, the aqueous phase was separated and the residual palladium concentration in the aqueous phase was determined, and from which the extracting rate of palladium was calculated to be 90.5%, where the total volume of the aqueous phase was given as 11.72 mL; the palladium in the organic phase was eluted with equal volume of ammonia water to determine the palladium concentration in the obtained eluted solution, from which the eluting rate of palladium was found to be 99.0%.

Application Example 10

0.72 mL of 1.50×10^{-2} mol/L sodium hydroxide was added to 10 mL material **3** to give a pH of 10.2 for the material solution, to which 10.00 mL nitrobenzene was added, followed by adding 1.00 mL of 0.20 mol/L potassium iodide, and after mixing to homogeneous, 10.00 mL of 2.484×10^{-3} mol/L B15C5-nitrobenzene was added; after agitating for 1min, the residual palladium concentration in the aqueous phase was determined, from which the extracting rate of palladium was calculated to be 96.0%.

Appendix 1: Compositions of material **1** and material **2**

① 元素	Na	Cs	Sr	Ba	Mo
② 含量，g/l	5.60	4.13	1.39	2.73	5.73
① 元素	Zr	Ru	Rh	Pd	La
② 含量，g/l	6.18	3.55	0.66	2.35	2.12
① 元素	Y	Nd	Ce	Fe	Ni
② 含量，g/l	0.78	6.92	4.40	5.04	0.35

③ 注1：料1内含硝酸3.52mol/l。

④ 注2：料2的成分与料1相同，除硝酸的浓度仍为3.52mol/l外，其余各组元的浓度均缩小一百倍。

Key:
1 Element
2 Content
3 Note 1: Material **1** contained 3.52 mol/L nitric acid. /1
4 Note 2: Material **2** had the same components as material **1**, and the concentration of nitric acid was also 3.52 mol/L, but the concentration of each element was reduced by 100-fold.

Appendix 2: the composition of material **3** is as follow: (mol/L):

① 硝酸根为	0.5	Na	5.1	Cs	示踪量②
③ 亚硝酸根为	2	Al	0.01	Ru	示踪量②
④ 碳酸根为	1	Rh	10^{-4}	Co	示踪量②
⑤ 硫酸根为	0.3	Pd	10^{-4}	Tc	微量⑥

⑦ 注：料3中pH值为11－12。

Key:
1 Nitrate ion
2 Trace amount
3 Nitrite ion
4 Carbonate ion
5 Sulfate ion
6 Micro amount
7 Note: pH of material **3** was 11-12

Appendix 3: Material **4** was a single palladium solution. The medium was blended to be 7.2 mol/L hydrochloric acid and 3.0 mol/L sulfuric acid in accordance with the needs of the study objective.